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               TESTING IODIZED ACTIVATED CARBON FILTERS WITH NON-RADIO ACTIVE -- TC(U)
               MAY 80   V R DEITZ, J B ROMANS
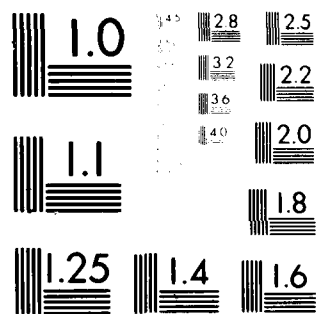UNCLASSIFIED   NRL-MR-4240   NL

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NRL Memorandum Report 4240

Title: Testing Iodized Activated Carbon Filters with Non-Radioactive
        Methyl Iodide

Authors: Victor R. Deitz and James B. Romans

Date: May 30, 1980

Page 2, line 12. . . . . $\dfrac{^{131}I}{^{127}I} = \dfrac{(2 \times 3.7 \times 10^4) \times (1 \times 10^6)}{\dfrac{1.75 \times 3}{142} \times 6.02 \times 10^{20}} \cong 3 \times 10^{-9}$

$3.7 \times 10^4 \text{dps} = 1\,\mu\,\text{Curie}$

$1 \times 10^{-6} \text{sec}^{-1} = \text{decay constant of } ^{131}I$

$142 = \text{molecular weight of } ^{127}I\text{-CH}_3$

Page 3, line 10. . . . . 10^9 parts instead of 10^{15} parts

Page 25, line 7. . . . . 10^9 instead of 10^{15}

Page 37, line 4 from bottom. . . 10^{-9} instead of 10^{-15}

Page 47, line 4 from bottom. . . 10^9 instead of 10^{15}

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Iodized carbons, impregnated with KI_x ($KI + xI_2$), were evaluated for trapping methyl iodide-127. In this method the complete effluent of the carbon is sampled and analyzed continuously. In contrast, the RDT-M16 test procedure counts the carbon and the back-up beds for the accumulated 131 species and no information is obtained for the interaction of the large amount of carrier methyl iodide-127 with the iodized charcoal.

The test apparatus to measure the penetration of methyl iodide-127 is described and the calibration procedures are detailed.
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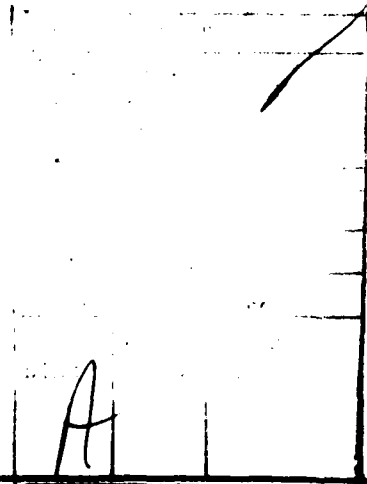1 JAN 73
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20. Abstract (Continued)

Results are given for the penetration of methyl iodide-127 through new activated carbons, carbons in service, and exhausted carbons withdrawn from service.

The reduction in trapping efficiency with service is accompanied by the development of a maximum in the concentration of methyl iodide-127 during the air purge after the dose period. This behavior has escaped notice with methyl iodide-131 due to the way that test is made.

The chromatographic holdup of methyl iodide-127 by carbons in service, together with the subsequent slow desorption step, could result in a dilution of the penetrating iodine to acceptable levels under some conditions encountered in plant filter operations.

Since testing procedures using iodine-131 have always been pursued in the presence of about 10^{15}-fold excess of iodine-127 in the gas phase, the question can be raised what would happen in a carbon filter in an accident mode when the carbon is subjected to 100% iodine-131. The present results suggest that the behavior would resemble that reported herein using the iodine-127 species. The bleeding behavior of the carbon filters at Three Mile Island and the laboratory behavior with methyl iodide-127 substantiate this thesis. One conclusion that appears valid is that both techniques, methyl iodide-131 by counting and methyl iodide-127 by chromatography are of value for testing carbon filters. The latter would supply the operational and maintenance information required for positive safety conditions.

Contents

Foreword

NRL Annual Report for ID 4.6.3.3 JM Iodine Filter Test

The Annual Report of the NRL investigations on charcoal for FY79
is in two parts. Part I, printed as a separate NRL Memorandum Report
4179, is concerned with the dust attrition of granular activated carbons.
The attrition is based on the small movements of particles relative to
each other and to a complex wear mechanism involving the frictional
forces between particles. This is different from the Ball and Pan
Hardness Test which entails the breaking and crushing of individual
particles.

The present report, Part II, is concerned with the rationale for
the use of ^{127}I-CH$_3$ as a test gas in a determination of the capability
of a carbon filter to adsorb iodine species and also for an estimate of
the residual life of a carbon filter. A description is given of the
procedure and calibration of the test equipment. Results are discussed
for new charcoals, charcoals in service, and for exhausted charcoals
obtained from several utilities.

TESTING IODIZED ACTIVATED CARBON FILTERS WITH NON-RADIOACTIVE METHYL IODIDE

I.   Introduction

The approach adopted in this study with the objective of testing carbon filters in place was first to determine the capability of the carbon sample (removed from full-scale systems) to remove ^{127}I-CH$_3$ and then to measure the residual efficiency of the filter, also using ^{127}I-CH$_3$. The observed behavior of iodized carbons to be described has raised serious questions regarding the stability of KI$_x$ impregnated charcoals in service and has delayed the completion of in-place tests on full-scale carbon filters.

The proposed test has both advantages and disadvantages. In the use of a non-radioactive test procedure, a detection of ^{127}I-CH$_3$ by chromatography is blind to the presence of a radioactive species. Conversely, however, a radioactive counting technique is blind to the detailed chemistry of the adsorbing surface of an iodized charcoal, only fractionally populated by ^{127}I. A test confined to ^{131}I counting can fail to give the correct prognosis of the behavior of the carbon filter in future service.

It is the sensitivity and stability of the present-day electron capture detectors for stable iodine that make low-level, in-line, measurements feasible (1). Radioactive counting techniques require the accumulation of the disintegrating species over a specified time, followed by transportation to a counter. The large difference in the magnitude of ^{127}I and ^{131}I involved in a test using radioactive techniques may be shown by a typical penetration test for methyl iodide at 30°C (2). The content of ^{131}I-CH_3 in the dose of the RDT M16 test is about two microcuries. The carrier concentration of ^{127}I-CH_3 is maintained at 1.75 mg/M^3 for two hours ($3M^3$). Hence, the mole ratio of the two species in the total dose is:

$$\frac{^{131}I}{^{127}I} = \frac{2 \times 3.7 \times 10^4 \text{ (}\mu\text{moles} \sim \text{d.p.s.)}}{\frac{1.75 \times 3}{142} \times 6.02 \times 10^{20}} \cong 3 \times 10^{-15}$$

(3.7 $\times$ 10^4 dps = 1 μ Curie; 142 = molecular weight of ^{127}I-CH_3)

When an iodized charcoal ($K^{127}I_x$ impregnation) is challenged with the above test mixture, the ^{127}I of the impregnation interacts with the large concentration of ^{127}I in the dose as well as with ^{131}I of the challenge. The counting results for a typical test (NRL 5118-3) are:

Sample Bed	1.21µCi	= 4.477 $\times$ 10^4 dps
Back-up Bed - A	0.0343µCi	= 1.27 $\times$ 10^3 dps
Back-up Bed - B	0.00264µCi	= 9.77 $\times$ 10^1 dps
Penetration	=	2.96%

Actually, there was 10^{15} more ^{127}I-CH_3 in the challenge than ^{131}I-CH_3; ^{127}I-CH_3 was therefore the dominant reactant in the adsorption process.

The iodized charcoal bed must play its role at all times as a positive safety protection against the emission of ^{131}I in an assumed accident mode. Consider the following three types of insult to an iodized charcoal:

Case   I $^{131}I-CH_3$ + $^{127}I-CH_3$ + ^{127}I - charcoal

Case II $^{127}I-CH_3$ + ^{127}I - charcoal

Case III $^{131}I-CH_3$ + ^{127}I - charcoal

Case I is the reactant situation in the present RDT M16 test procedure and, as mentioned above, the iodized charcoal is contacted by the mixture of 10^{15} parts $^{127}I-CH_3$ to one part $^{131}I-CH_3$ and the test bed and the back-up beds are then counted. Case II is the situation presented in this report in which the iodized charcoal is contacted with 100% $^{127}I-CH_3$ and the gaseous effluent is continuously analyzed for $^{127}I-CH_3$ by chromatography with an electron capture detector. Case III is an important accident situation for which the carbon filter was designed, namely to trap ^{131}I. In Case I the gaseous reactant mixture supplies ^{127}I in large concentration to reactant sites on the charcoal where a possible isotope exchange can take place; in the real situation of Case III, only the ^{127}I of the charcoal is available for exchange. This report considers the possibility that Case II may be more relevant than Case I to an accident mode (Case III). Note that in the RDT test, the carbon is counted; in Case II one analyzes the gaseous effluent directly and continuously.

An estimate can be made of the surface coverage of an activated carbon by an iodide impregnation. For the calculation a carbon surface area of 1000 M^2/g is taken and an impregnation of 2 wt.% iodine ion is

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considered. The latter corresponds to 157 μmoles of I^- per gram of charcoal. Since the ionic radius of the iodide ion is 2.228 $\overset{o}{A}$, the fractional surface coverage is:

$$\frac{157 \times 6.02 \times 10^{17} \times \pi \ (2.228 \times 10^{-8})^2}{1000 \times 10^4} = .015$$

Hence, if the iodine ion has a statistical monolayer thickness, the coverage is 1.5%. The coverage is less if the impregnation is in the form of small 3-dimensional crystallites.

The iodine isotopes produced by the fission of ^{235}U, for which the half-lives are greater than about one minute, are given in Table 1. The stable isotope, ^{127}I, is produced in small quantities (1/20th that of ^{131}I). However, in fuel elements that have received long service, the predominant iodine species will be ^{129}I and ^{127}I.

Table 1:   Iodine Isotopes Produced by the Fission of ^{235}U
(Percent of Fission Products)

Isotope	Initial Products	Half Life
137	6.2%	24.6 sec
136	6.12	85.0 sec
135	6.2	6.6 hr
134	7.2	52.6 min
133	6.7	20.8 hr
132	4.3	2.3 hr
131	2.9	8.04 day
129	0.72	10^7 years
127	0.12	stable

G.E. Chart of the Nuclides, April 1977

Walker, F. W., Kirouac, G. J. and Rourke, F. M.

II. Rationale for a Non-Radioactive Test Procedure

The ability to make on-line penetration measurements with $^{127}I\text{-}CH_3$,
as mentioned above, has several advantages. The necessary health physics
requirements for radioactive materials would be eliminated and continuous
monitoring of a filter would be without restrictions. Each $^{127}I\text{-}CH_3$
measurement requires about five minutes and a charcoal sample may be
withdrawn anytime after the measurements. When $^{131}I\text{-}CH_3$ is used in a
test, any subsequent storage of the charcoal must be delayed until the
radioactivity decays. The cost of the chromatograph and detector compares
favorably with that involved in handling and counting ^{131}I. In normal
plant-scale operations, very low-level (10^{-12} microcurie/cc) radio-
iodine is present. This means that determinations based on counting
the inlet and outlet air flows require a sampling time of not less
than 24 hours in order to use counting times of about 1000 seconds.
In contrast, a chromatographic result with $^{127}I\text{-}CH_3$ requires five
minutes using a calibrated electron capture detector.

The background concentration of methyl iodide in the outdoor
environment is very low, a value of 5 ± 3 ppt has been reported (3) in
a marine interface, but this disappeared in overland masses. However,
the common contaminants of ventilation air, such as nitrogen oxides,
sulfur dioxide, ozone and total hydrocarbons, being retained by the char-
coal, influence the trapping mechanism and are detrimental to the
trapping efficiency (17).

More than 15 years ago Adams and Browning (4) used elemental iodine
vapor ($^{127}I_2$) for in-place testing of the carbon filters on the NS

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Savannah. Normal iodine was preferred over ^{131}I because of possible

contamination of the ship. Separate tests, however, were made with and

without ^{131}I. The dose was 1 to 3 g of elemental ^{127}I and the effluent

samples were flown to the laboratory for activation analysis. The dose

of ^{131}I was 5 to 15 millicuries and the back-up beds from the test were

counted aboard. Reasonable agreement between the two procedures was

found by Adams and Browning (4), see Table 2.

Table 2: In-Place Tests with Iodine (I_2) on NS "Savannah"
by Adams and Browning (4)

Test	$^{127}I_2$ Injected g	Iodine Efficiency (%)	Test	^{131}I mc	^{127}I mg	Iodine Efficiency (%)
2	1.6	99.9$^+$	6	15	2	99.99$^+$
3	1.2	99.9$^+$	7	15	2	99.99$^+$
5	1.4	99.9$^+$	8	7	3	99.97$^+$
6	1.6	99.9$^+$	9	7	3	99.97$^+$

Additional measurements were reported by Thomson and Grossman (5),

see Table 3, with similar results.

Table 3: In-Place Testing with Iodine (I_2) Removal on NS "Savannah"
by Thomson and Grossman (5)

Date	Isotope	Penetration
2 July 1965	^{127}I	0.072%
5 July 1965	$^{131}I + ^{127}I$	0.012%
7 July 1965	^{127}I	0.093%
7 July 1965	^{127}I	0.032%
31 May 1965	$^{131}I + ^{127}I$	0.017%

Billard and Brion (6) preferred elementary iodine rather than methyl iodide for in-place testing, but gave no numerical results. Gukeisen and Malaby (7) reported in-place testing of carbon filter banks at ALRR using (a) spectrophotometric, (b) neutron activation, and (c) counting of $^{127}I_2 + ^{131}I_2$. The lower results in Table 4 were explained by the presence of methylchloroform and methyl alcohol producing organic iodides in the source solutions in (a) and (b). The $^{131}I_2 + ^{127}I_2$ in (c) was generated as a vapor. See also reference (8).

Table 4: Iodine (I_2) Trapping Efficiency at Argonne
Laboratory Research Reactor (7)

Filter Bank	Spectrophotometric (%)	Neutron Activation	$^{131}I_2$
Exhaust, Top	99.2	99.3	>99.99
Exhaust, Bottom	99.3	99.35	>99.99
Water Seal Exhaust	99.8	99.95	–

Swanks (9) reported several interesting in-place tests with $^{131}I_2$ and $^{130}I-CH_3$ (both with ^{127}I) added simultaneously to the SBHE carbon filters at Oak Ridge. The results (Table 5) show high efficiency in both cases. It is to be noted that new carbon only was present in the carbon filters and the relative humidity was not given.

Table 5: Iodine Removal with Carbon Filters in SBHE (Special
Building Hot Exhaust) at the Oak Ridge National Laboratory (9)

System	$^{131}I_2$ (%)	$^{130}I-CH_3$ (%)
East	99.994	99.97
Standby	99.994	99.97
West	99.995	99.98

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The pioneering studies on radioiodine removal at the Oak Ridge National Laboratory were reported in numerous publications over the period 1960–1970. These have been studied and those pertinent to the present subject and which contain primary results are given as references. The presence of chemical species other than elemental iodine was soon established. Methyl iodide was identified as the principle compound and has since been adopted as a test gas. One of the earlier reports on in-place filter testing with ^{127}I-CH$_3$ was that of McFee and Bechtold (10) at the Argonne National Laboratory. A pyrolyzer and the Mast Microcoulomb Detector was used. These authors reported that the advantages of the procedure were found to outweigh the disadvantages. However, no comparison was reported with ^{131}I-CH$_3$ and, most important, no variation was made in the status of the carbon in the carbon filter. In all of the above examples, the carbons were either new or nearly-new material.

III. Measurements

3.1 Scaling Factors

Two dynamic test apparatus were constructed to study the penetration of non-radioactive methyl iodide. The scaling factor retained the RDT-M16 specification for linear flow, namely 12.2 m/min. (40 feet/min.) and the residence time of 0.25 seconds (2). A comparison is given below:

	RDT-M16	NRL Laboratory	
		Small Bed	Large Bed
Bed diameter (cm)	5.08	2.54	26.7 x 26.7
Bed height (cm)	5.08	5.08	5.08
Linear air velocity (m/min)	12.2	12.2	12.2
Residence time (sec)	0.25	0.25	0.25
Volume flow (liters/min)	25	6.2	880.
Total methyl iodide (mg)	5.25	1.31	185.
Temperature °C	30	30	30

The air flow (6.2 ℓ/min) passed in sequence (Figure 1) through: (1) regulator and control valve(s), (2) dry test meter (American DTM 115), (3) particulate and charcoal filter, (4) humidifier, (5) electric hygrometer element, (6) mixing chamber, (7) gas sample opening to chromatograph, (8) thermostated container for the charcoal sample, (9) exit to detection elements, (10) exit to trap and vent. The cylindrical tube (8) was maintained at constant temperature by a surrounding resistance heater with the controlling thermocouple located beneath the center of the bottom perforated plate holding the charcoal. Additional thermocouples were located at the center of the bottom charcoal support and at the top center of the charcoal. The air flow could be directed either upward or downward through the charcoal. A mixture of methyl iodide and nitrogen was pressurized in a stainless steel bottle and
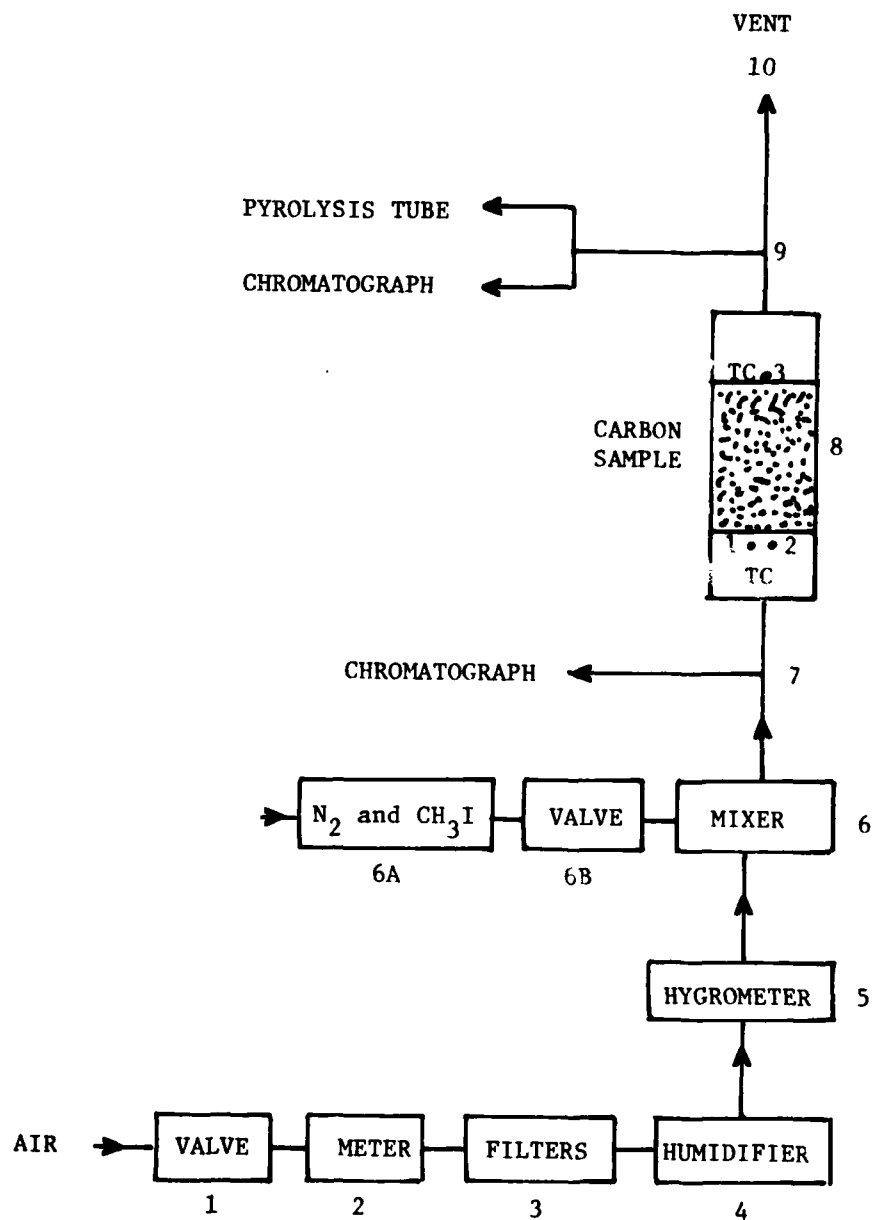
Figure 1. Flow diagram for ^{127}I-CH$_3$ experimentation with small carbon bed (2.54 cm dia x 5.08 cm high).
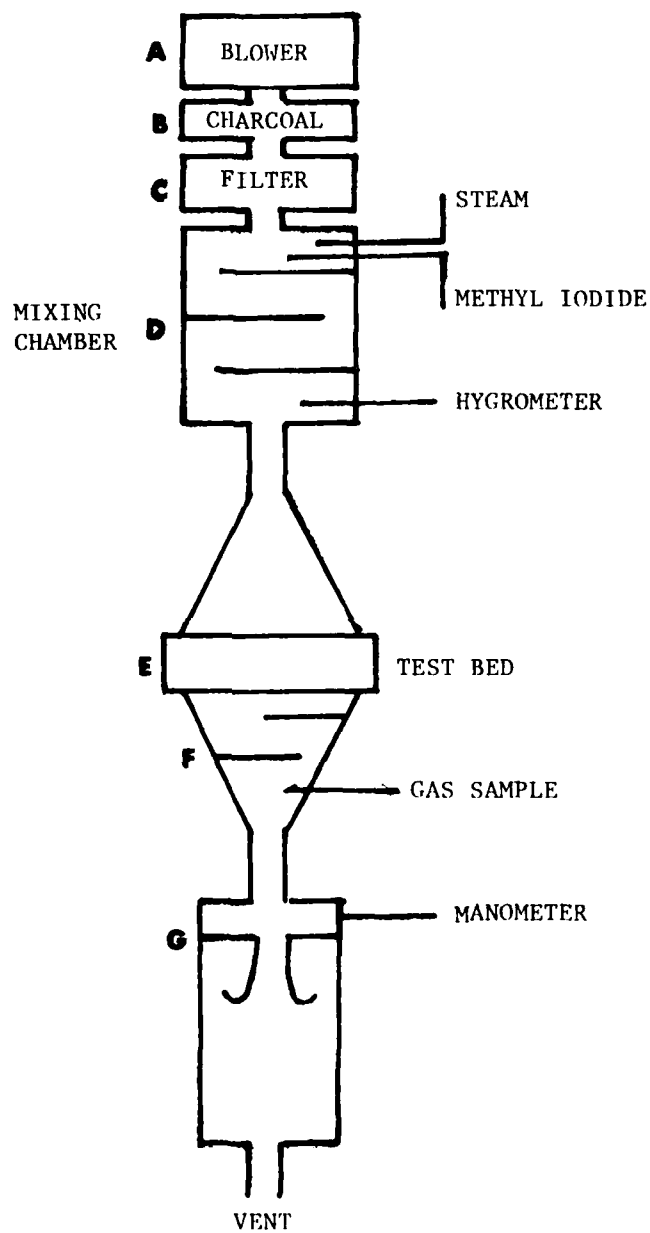
Figure 2. Flow diagram for $^{127}I\text{-}CH_3$ tests with large carbon bed
(26.7 cm x 26.7 cm x 5.08 cm).

metered as desired into the mixing chamber through a pressure regulator and a microneedle valve.

The air flow (880 ℓ/min) of the larger unit (Figure 2), generated by a GAST regenerative blower, A, was passed through a charcoal unit (26.7 x 26.7 x 5.08 cm)B, and a particulate filter (26.7 x 26.7 x 15.2 cm)C. It then entered a mixing chamber, D, of stainless steel with baffles where the required steam was added to attain 90% RH. Also added was the desired dose of ^{127}I-CH$_3$ and any air contaminant desired in the study. The mixture was then directed to the test charcoal, E, after which it passed through a mixing cone, F, and was sampled for chromato-graph or the MAST detector. The flow was measured at the outlet by the pressure drop across a calibrated orifice, G.

3.2 Calibration of the Gas Chromatographs

The basic gas chromatograph used for the analysis of low level ^{127}I-CH$_3$ was a Hewlett Packard Model 5730A. In the electron capture detector, a ^{63}Ni radioactive source is plated on the interior surface of one-half the cell and the beta emission results in the formation of many secondary electrons from the carrier gas (argon/methane). A potential is pulsed across the cell (frequency modulation) to maintain a constant value during passage of the flow through the cell. The change in pulse frequency is then proportional to concentration of the sample introduced. A PORAPAK column (3' x 1/8") was used with the oven at 100°C.

The standard in the calibration for methyl iodide was a calibrated permeation tube No. 4131 (AID). When maintained at 30°C ± 0.10, the weight loss was 270 nanograms/minute. The concentration was varied by adjusting the flow rate past the tube and additionally by double dilution

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with a second known air flow. The overall accuracy was limited by the precision with which the air flows could be measured. In the graph of the calibration (Figure 3), the peak heights at unit attenuation (Δ) are the Y-coordinates and the concentrations (C) in ppm (volume of methyl iodide per unit volume of air) are X-coordinates.

The data were represented by the following polynomial:

$$\ln C(\text{ppm}) = A_0 + A_1(\ln\Delta) + A_2(\ln\Delta)^2 + A_3(\ln\Delta)^3 \qquad (1)$$

$$A_0 = -11.22966$$
$$A_1 = 0.69774$$
$$A_2 = -0.002830$$
$$A_3 = 0.001452$$

The polynomial evaluation for equation (1) can be conveniently and rapidly made on a TI 59 Programmable Calculator which includes the necessary built-in standard solid state software module.

The reproducibility of the calibration was excellent. Air samples into the sampling loops of the chromatograph have been withdrawn from a large number of tests using both new and weathered charcoals. The standard operating procedure was to direct the column effluent to a flame ionization detector and at a specified effluent time to switch to the electron capture detector. This precaution offered maximum protection of the electron capture detector in maintaining the calibration for the methyl iodide peak. The double circle in Figure 3 refers to two calibrations taken three months apart.

An independent detector for elemental iodine was also used in the charcoal effluent stream. This was a modified microcoulombmeter (Mast
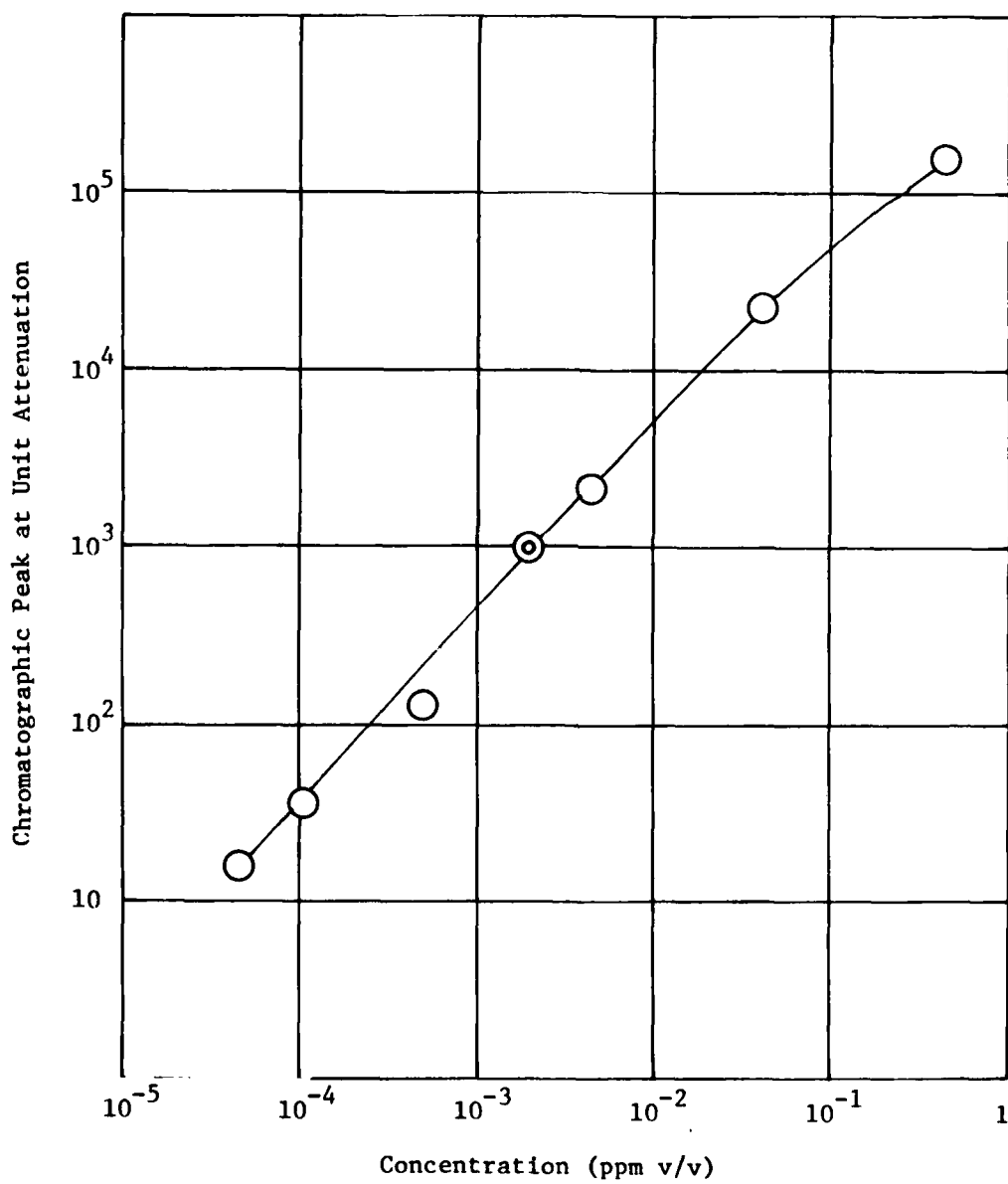
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Figure 3. Calibration curve for $^{127}I\text{-}CH_3$ using chromatograph with electron capture detector.
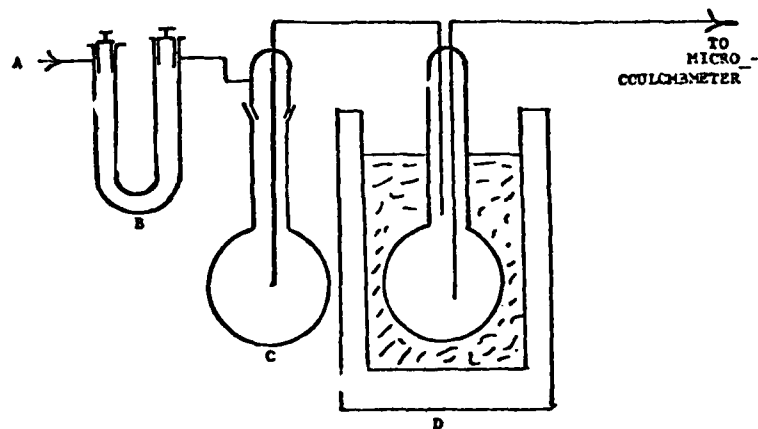
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Figure 4. Calibration source for dry air and iodine vapor
using iodine crystals at constant temperature.

Instrument Co. Model 724-2). Two independent calibrations of this instrument were made. One was based on the known vapor pressure of iodine crystals and the second on the quantitative pyrolysis of the methyl iodide delivered from the certified permeation tube. Figure 4 is a schematic flow diagram of the calibration source of air + iodine vapor. Air was passed through charcoal and drierite and at position A entered the tube B containing Anhydrone (barium perchlorate). The dried air was then passed over iodine crystals in flask C at room temperature and then into a second flask, D, held under the liquid level of a cryostat maintained at the desired temperature. Thus, the approach to the equilibrium vapor pressure of iodine was from a higher vapor pressure, a procedure found necessary to attain steady states.

The published data for the vapor pressure of iodine crystals at and below room temperature were reviewed and a least square linear regression analysis gave the following:

$$\ln P_{I_2} \text{ (torr)} = -8148.4/T°K + 26.361 \tag{2}$$

The output of the microcoulombmeter was shunted across a resistance of 5250Ω and the voltage drop (mv) was recorded. A plot of ln $\underline{mv}$ was made as a function of the reciprocal cryostat temperature (°K); a least square linear regression analysis gave:

$$\ln \underline{mv} = 6663/T + 31.736 \tag{3}$$

Combining equations (2) and (3) the following calibration formula was obtained:

$$\ln P_{I_2} = 1.2229 \ln mv - 12.449 \tag{4}$$

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The second calibration was based on the formation of I_2 in the pyrolysis of methyl iodide in an air flow. It was necessary to regulate the temperature of the quartz tube within a narrow range in order to obtain quantitative decomposition. The desired mechanism is given by:

$$2 \text{ CH}_3\text{I} + \frac{7}{2} \text{ O}_2 \rightarrow \text{I}_2 + 3\text{H}_2\text{O} + 2\text{CO}_2$$
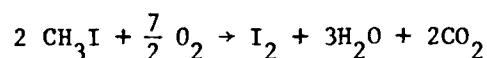
When the temperature of pyrolysis is too high, a second mechanism of decomposition occurs, i.e.

$$2 \text{ CH}_3\text{I} \rightarrow 2 \text{ HI} + \text{C}_2\text{H}_4$$
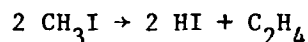
When the tube furnace around the quartz tube was held at $650 \pm 20°C$ (inside temperature of the tube), the conversion was practically quantitative (Table 6). A plot of methyl iodide introduced (ppm) as a function of iodine produced gave a slope of 2 in agreement with theory.

Table 6: Pyrolysis of Methyl Iodide-Air Mixtures at Optimum Temperature of 650°C

Mast Microcoulombmeter Iodine (I_2)		Calcd. from Permeation Tube	% Conversion
(mv)	ppm		
3.14	.063	.073	87
3.82	.081	.087	93
4.74	.105	.106	99
4.91	.109	.114	96
4.89	.109	.115	95
4.86	.108	.116	93
9.05	.161	.162	99
9.20	.164	.162	100
9.37	.168	.162	100
9.0	.160	.162	99
9.0	.160	.161	99
3.54	.073	.075	99

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The certified permeation tube containing liquid methyl iodide was also used to calibrate a modified Hewlett-Packard gas chromatograph (5710 A series) equipped with a flame-ionization detector and a 10% DC 200 Chrom G 80/100 column (5' x 1/8") with the oven at 100°C. This chromatograph was used to determine inlet concentrations of $^{127}I-CH_3$. The air flow across the permeation tube (maintained at 30°C) was varied 100-fold and the corresponding chromatographic peak heights (h) were measured. Typical data and the calculated concentration, $\underline{c}$, at 25°C are given in Table 7. A least squares linear regression analysis gave the following relationship:

$$\underline{c} \text{ (ppm)} = 0.342 \, \underline{h} - 0.139 \tag{5}$$

In order to realize a dose of methyl iodide of 1.31 mg in two hours (1/4 the dose of the RDT test for a 2-inch diameter column), an average con-concentration of 0.30 ppm (V/V) would have to be maintained. At unit attenuation this concentration corresponded to a peak height of 20.5 chart divisions.

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Table 7: Calibration of Gas Chromatograph (HP 5710) with a Certified
Permeation Tube of Methyl Iodide (30.0°C)

Air Flow ml/min	Concn. ppm	Peak Height (attenuation 16) chart-divisions
199	0.23	0.4
203	0.23	0.3
56.7	0.82	1.9
20.9	2.23	6.5
9.80	4.75	14.1
7.01	6.63	19.8
3.64	12.8	36.8
31.7	1.45	5.6
12.3	3.74	13.9
12.7	3.63	13.7
5.2	8.85	28.4
13.4	3.44	10.1
2.6	17.4	51.6
3.6	12.8	34.6
58	0.79	1.4

IV. Results

4.1 Penetration of ^{127}I-CH$_3$ through New Activated Carbons

The penetration data as a function of time (or flow) can be presented in terms of concentration or as the accumulated methyl iodide in the effluent up to the specified time. A total time of 120 minutes is required to make comparisons with independent results on the same carbon using ^{131}I-CH$_3$ in which the accumulated iodine is counted (2).

One of the first comparisons was made for a new carbon sample with and without prehumidification of the carrier air for 16 hours at 90% RH. Previous work had shown that the penetration using ^{131}I-CH$_3$ increased with the time of prehumidification. The dose period and the subsequent purge was always conducted with air at either 90 or 95% RH. The results given in Figure 5 were first reported at the 15th DOE Air Cleaning Conference (1). For any given time the penetration after prehumidification was significantly greater than for the non-prehumidified sample. The penetration of ^{127}I-CH$_3$ was calculated for a given time, t, as follows:

$$\text{penetration (\%)} = \frac{100 \times \text{Summation of Effluent to time t}}{\text{Summation Introduced to time t}}$$

The point "R" in Figure 5 corresponds to the independent determinations using ^{131}I-CH$_3$ with the RDT, M16-IT test procedure. The agreement was very satisfactory when the comparison was made at 120 minutes which corresponds to the dosing period of the ^{131}I-CH$_3$ test. It may be noted in Figure 5 that the dose period in the ^{127}I-CH$_3$ test with prehumidification was 120 minutes, but the dose period in the test without prehumidification was extended to 180 minutes.
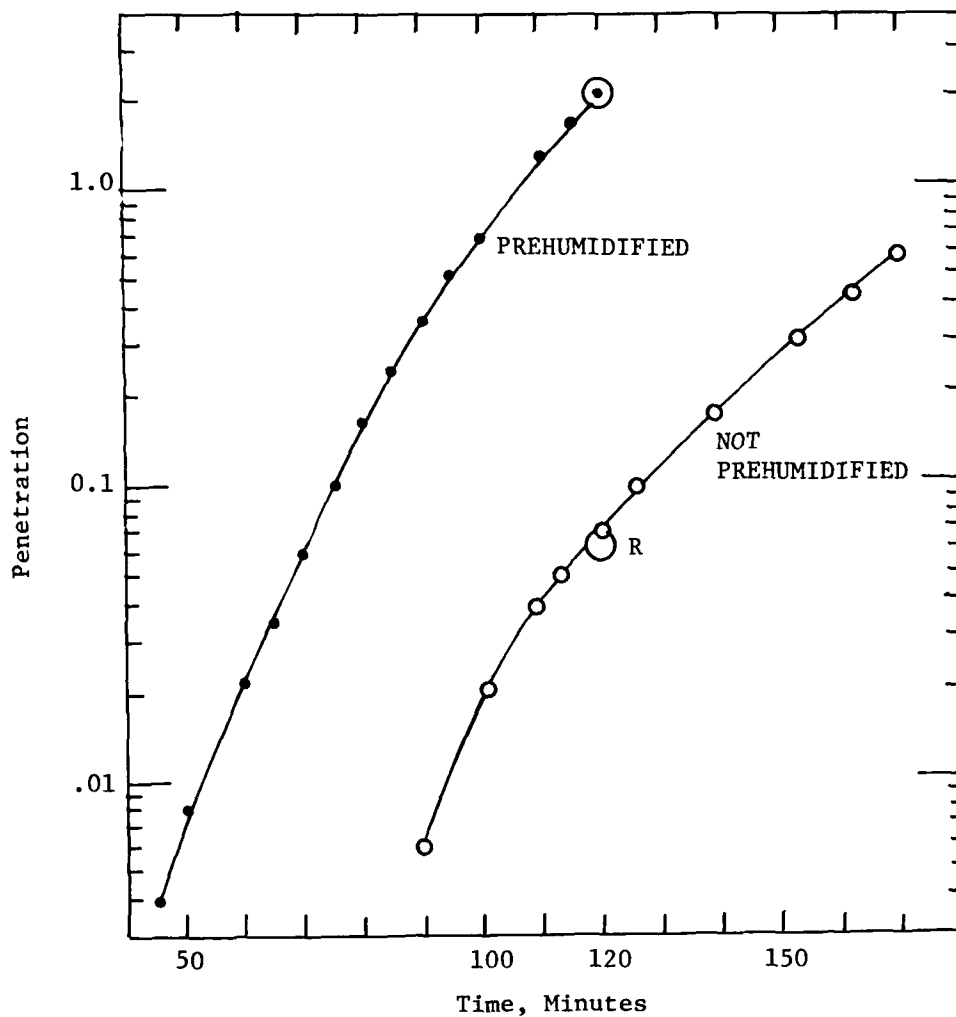
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Figure 5. Penetration of methyl iodide-127 through BC-727 in 90% RH air with (Test 3287) and without (Test 3283) prehumidification. Note: R signifies independent results with $^{131}I-CH_3$.

Similar results for additional new charcoals (summarized in Table 8) indicate that the penetration was independent of the methyl iodide concentration over a 2-fold range. The reaction appeared to be first order in methyl iodide in that the rate was independent of inlet concentration. Other factors than inlet concentrations, however, are rate determining in the trapping mechanism. In a comparison with the results using ^{131}I-CH$_3$ the dose level of the latter was independent of small changes in ^{131}I-CH$_3$ concentration. This behavior may be due to the relative very small influence on the ratio ^{131}I-CH$_3$ to ^{127}I-CH$_3$, which is approximately 10^{-15}.

The charcoals listed in Table 8 were all new materials. (See Appendix 1 for a listing of charcoals used in this report.) BC-727 and NACAR-615 are commercial charcoals and 4314, 4315, and 4316 are laboratory impregnations using KI, KIO$_3$, hexamethylenetetramine and a pH 10 phosphate buffer (11). The agreement between the penetrations with ^{131}I-CH$_3$ and ^{127}I-CH$_3$ at 120 minutes is rather good. Insofar as new charcoals are concerned, the use of ^{127}I-CH$_3$ is a feasible test gas to evaluate penetration at 120 minutes.

It is important to note that identical results are obtained using either the MAST microcoulombmeter or the chromatograph with the electron capture detector. An example is given in Figure 6, also for a new charcoal (NUCON KITEG II). The dose during 120 minutes was monitored (top of Figure 6) with the Hewlett-Packard 5710A chromatograph with the flame-ionization detector. The effluent concentrations were determined with the Mast (points ⊙) and with the electron capture detector (points X). The ordinate of Figure 6, concentration of ^{127}I-CH$_3$ (mg/M^3), drops sharply at the end of the dose period and at these points could only be

Table 8: Summary of Carbon Penetrations at 120 Minutes for ^{131}I-CH$_3$ and ^{127}I-CH$_3$ in 90% RH Air Using Five New Carbons

Charcoal	Procedures	Prehumidi- fication	Test	Introduced n moles	Penetration %
BC 727	CH$_3$I-131(EET)	yes		36900	2.2
	Non-radioactive	yes	3287	16600	2.1
	CH$_3$I-131(EET)	no		110700	0.056
	Non-radioactive	no	3283	26000	0.10
	Non-radioactive	no	3276	19300	0.14
NRL 4314	CH$_3$I-131(EET)	yes		36900	1.73
	CH$_3$I-131(NRL	yes		36900	1.54
	CH$_3$I-131(NRL)	yes		36900	1.82
	CH$_3$I-131(NRL)	no		36900	0.57
	Non-radioactive	no	3269	31100	0.38
	CH$_3$I-131(NRL)	no		36900	0.10
NRL 4315	CH$_3$I-131(EET)	yes		36900	0.14
	CH$_3$I-131(NES)	yes		36900	0.24
	CH$_3$I-131(NES)	yes		36900	0.53
	CH$_3$I-131(NRL)	yes		36900	0.26
	CH$_3$I-131(NRL)	no		36900	<0.01
	Non-radioactive	no	3285	18400	.008
NRL 4316	CH$_3$I-131(NRL)	yes		36900	0.90
	Non-radioactive	no	3286	16600	0.10
	CH$_3$I-131(NRL)	no		36900	0.051
NACAR 615	CH$_3$I-131(NRL)	yes		36900	0.27
	CH$_3$I-131(NRL)	no		36900	0.05
	Non-radioactive	no	3277	12900	0.00

EET - Environmental Engineering & Testing

NES - Nuclear Environmental Services

NRL - Naval Research Laboratory

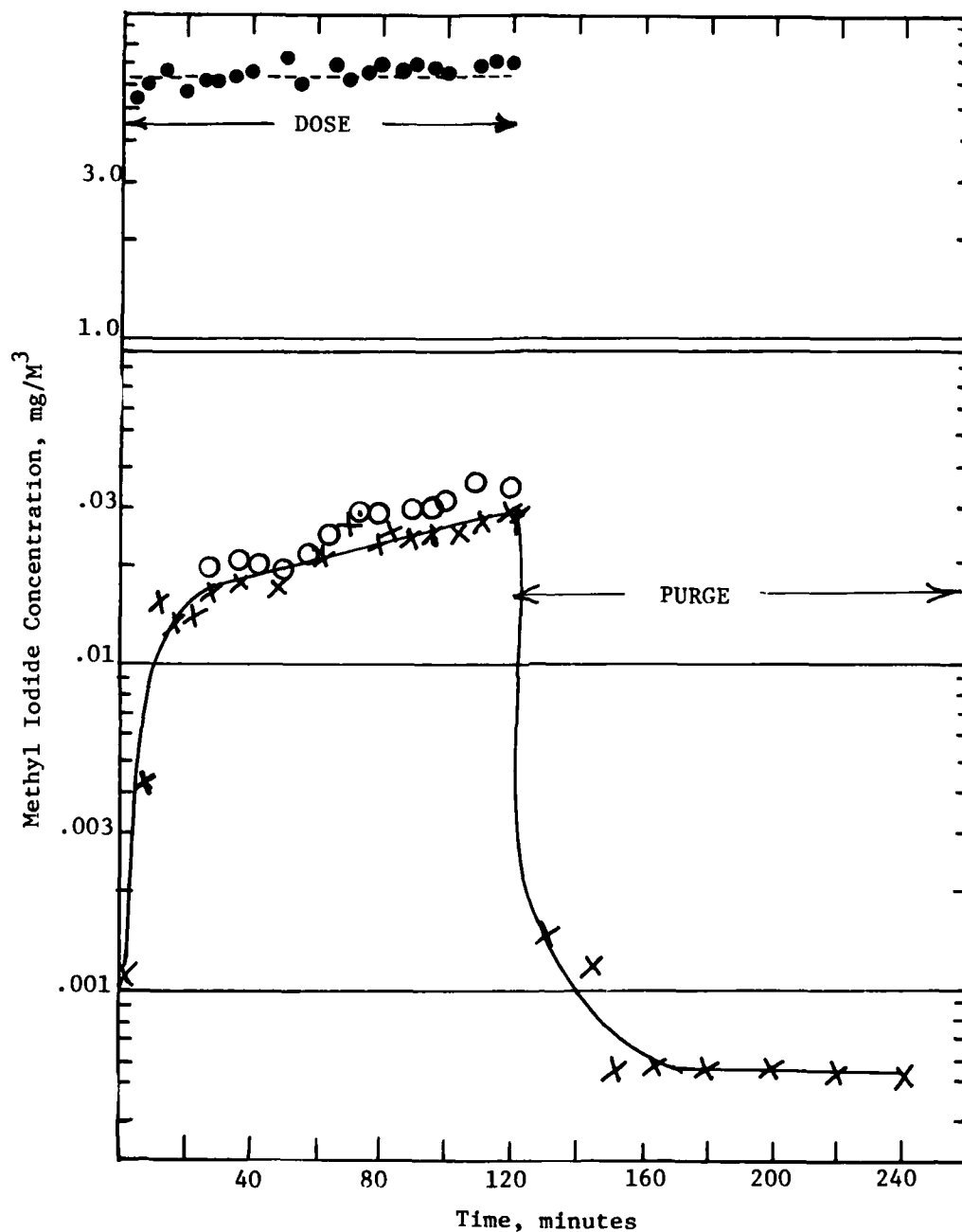Figure 6. On-line measurements of inlet and effluent concentrations of ^{127}I-CH_3 in air using new carbon (Nucon KITEG II) prehumidified 16 hours at 25°C and 95% RH (NRL Test 3320).

followed by the more sensitive electron capture detector. It will be

shown that this sudden decline may be characteristic of new or slightly

used carbons, especially those containing TEDA (triethylenediamine).

Insofar as new carbons are concerned, the agreement between

$[^{131}I\text{-}CH_3 + ^{127}I\text{-}CH_3]$ and $^{127}I\text{-}CH_3$ alone as test species indicates an

equal efficiency in removing both isotopes. As presented in the

Introduction, the ratio of $^{127}I/^{131}I$ in the dose is about 10^{15}; it is

not possible, therefore, to measure any $^{127}I\text{-}CH_3$ resulting from an

isotope exchange. This does not mean that an exchange of iodine

isotopes might not occur. The mechanism of the trapping of radio-

iodine is treated in detail in the Discussion.

4.2 Penetration of $^{127}I\text{-}CH_3$ through Charcoals in Service

The charcoal in a carbon filter is progressively modified by

continuous exposure to the contaminants of an air flow. One example

(Figure 7) compares the effluents from new G-615 and the same charcoal

weathered three months in a flow of outdoor air at NRL (Sample 5022).

The ordinate in Figure 7 represents the integrated $^{127}I\text{-}CH_3$ in the

effluent (microgram) during the dose period. The measurements in both

cases were with no prehumidification and, consequently, the penetration

after 120 minutes was quite small:

New G-615, not prehumidified	0.03%
3-month weathering, not prehumidified	0.15%

In both cases the concentration of $^{127}I\text{-}CH_3$ in the subsequent air purge

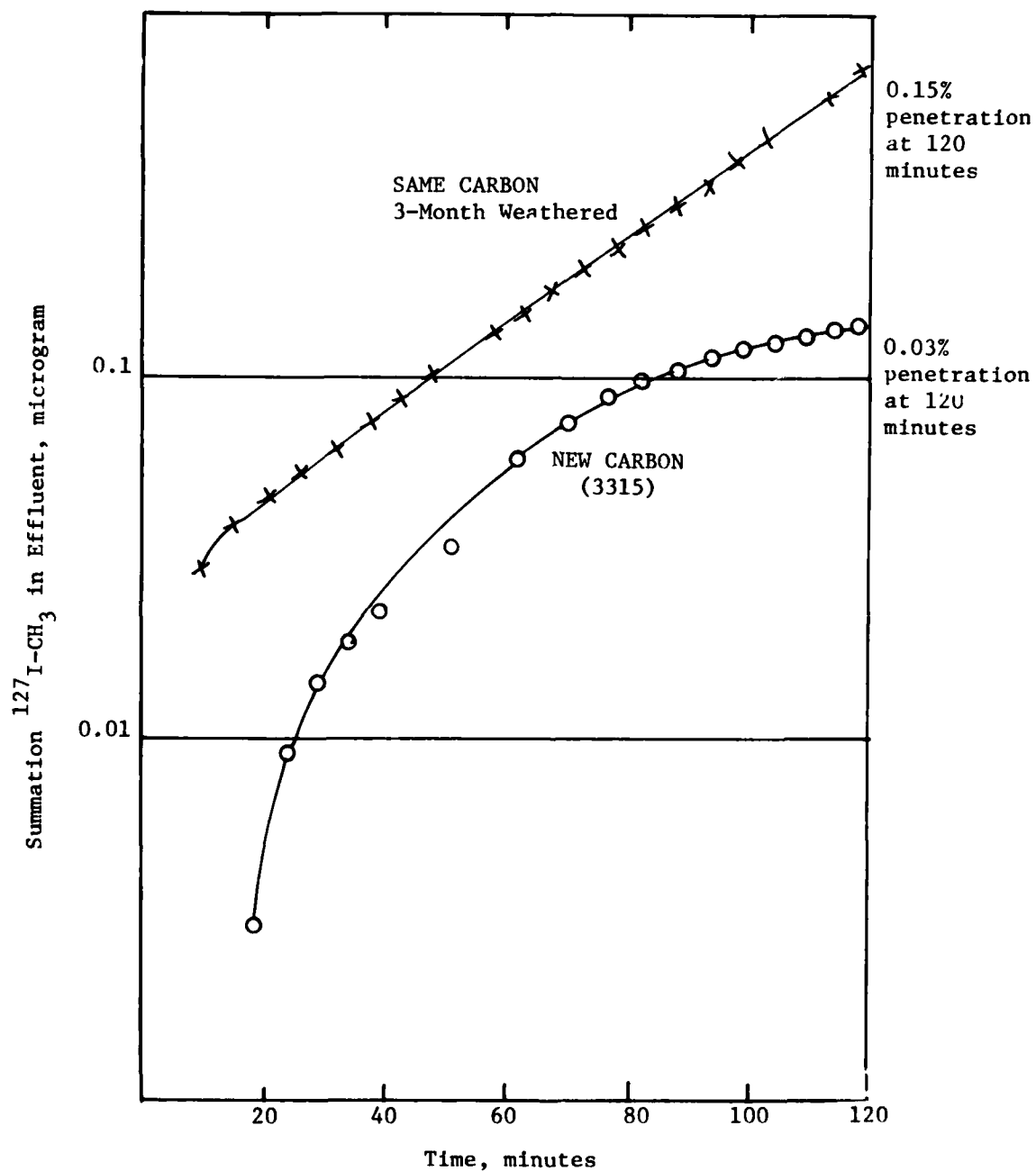following the dose dropped immediately to the baseline of the detector.

25

Figure 7. In-line measurements of ^{127}I-CH$_3$ through carbon
weathered 3 months in outdoor air compared with
the new material (NACAR G-615).

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4.3 Penetration of ^{127}I-CH$_3$ through Exhausted Carbons

A species which appeared in the chromatogram of the air purge from exhausted carbons (kindly supplied from electric utilities) was located at the identical position of known methyl iodide. When the sample was introduced into the test apparatus, the effluent during the first 20 minutes of air flow contained 3 to 4 ppb of ^{127}I-CH$_3$ and subsequently (see Table 9) decreased to about 0.06 ppb in 200 minutes (total air flow = 5M^3). A second carbon, which had been removed from a different facility, also showed about the same emission of ^{127}I-CH$_3$. The above low-level emission occurred before the dose of methyl iodide was introduced. It indicates the presence of some source of ^{127}I-CH$_3$, either desorbed from the carbon or readily decomposed from the impregnation of the exhausted charcoal, and appears when the samples are placed in a moving air stream. The above measurements before the admission of the dose serve as a control in establishing the base line.

Table 9: Initial Purge of Sample with Air Only for an Exhausted Carbon (NRL Sample 5149, Test 3331)

Time (Min)	MeI (mg/M^3)	ppb
1	0.018	3.1
6	.026	4.5
20	.0181	3.1
40	.00832	1.44
80	.00387	0.67
111	.00248	0.43
135	.00231	0.40
210	.00033	.057
405	.00050	.088
1400	.00026	.045

Air flow at V_ℓ = 12 m/sec, residence time 0.25 sec, and 90% RH

The role of relative humidity of the air flow is also highly critical in testing exhausted charcoals. A sample obtained in the replacement of a utility carbon bed (NRL 5144) was found to have a penetration of 11.5% using ^{131}I-CH$_3$ and 95% RH. This charcoal was tested using ^{127}I-CH$_3$ under the three conditions noted in Table 10. The prehumidification was made for 16 hours in one case and no prehumidification in two other determinations. The relative humidity during the dose and purge periods was 95% RH in two cases and 30% RH in one case.

Table 10: Penetration of ^{127}I-CH$_3$ Through Sample 5144

| Test | Pretreatment | Dose | | |
		RH %	Time (min)	Pene. %
3318	Prehumidified at 95% RH	95	120	13.7
3332	Not prehumidified	95	120	2.7
3339	Not prehumidified	30	120	.003

Contact time 0.25 sec; linear flow rate 12.2 m/min; temp. 30°C

The penetration of 13.7% may be compared with that obtained under the same testing conditions with ^{131}I-CH$_3$, namely 11.5%. The initial emission of ^{127}I-CH$_3$ during the 1400 minutes before the admission of the dose totaled only 0.011 mg. The total dose in Test 3318 (Table 10) was 3.76 mg ^{127}I-CH$_3$ in 120 minutes, and the total effluent was 0.516 mg. The initial emission before the dose is thus seen to be quite small.

The complete time dependence of penetration during the dose periods of Table 10 is shown in Figure 8. The penetration in air at 30% RH (Test 3339) was quite low and changed little during the dose period of 120 minutes, while the other two tests in air of 95% RH for the same
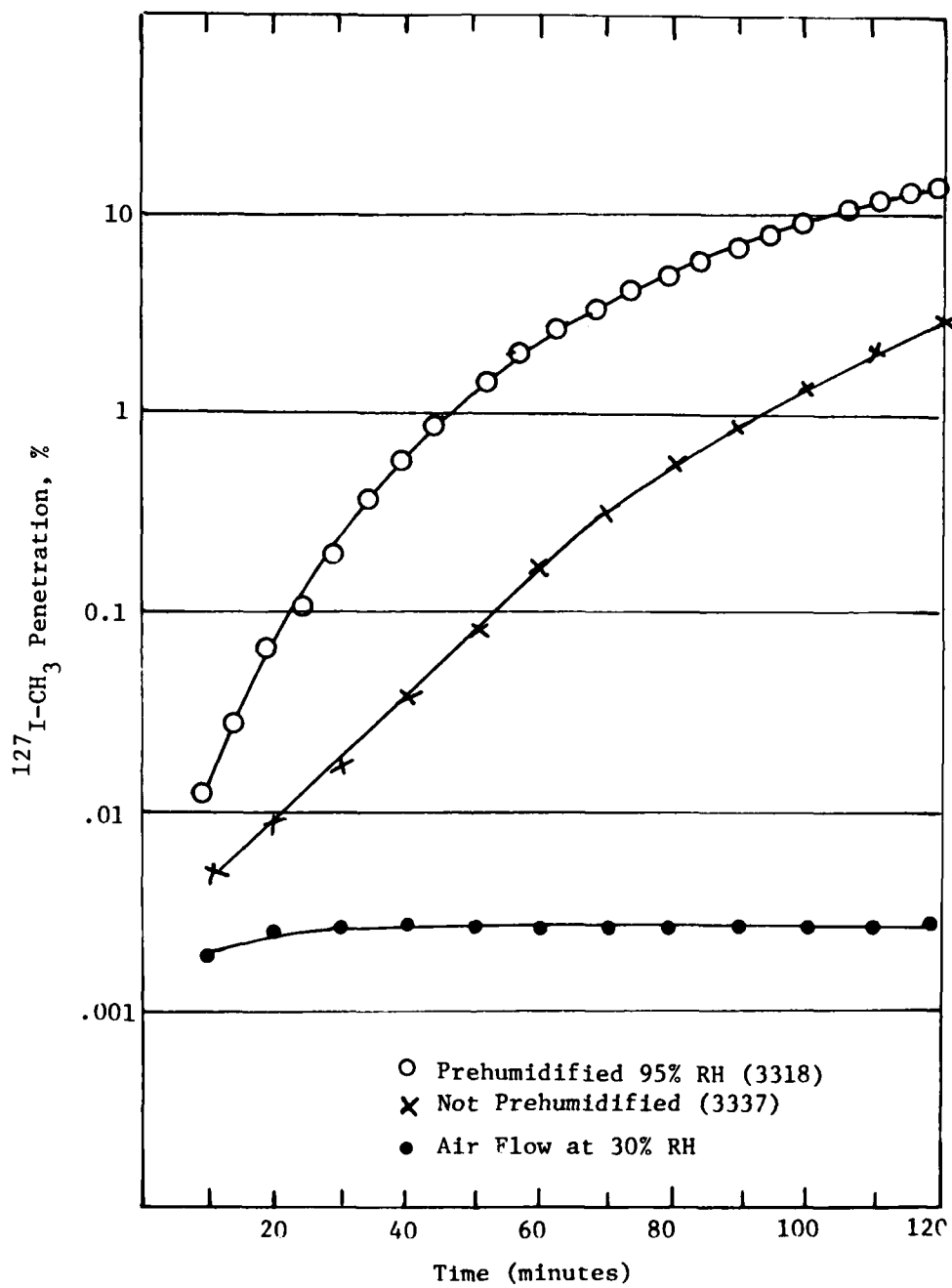
Figure 8. Penetration of ^{127}I-CH$_3$ through service charcoal NRL 5144.

carbon sample showed a characteristic sigmoid curve over a similar dose period. The ordinate of Figure 8, defined as in Section 4.1, is based on the ratio of summation of ^{127}I-CH$_3$ in the effluent to time t divided by the summation of that introduced to time t. The high trapping efficiency of an exhausted carbon at 30% RH and the low efficiency at 95% RH presents an insight as to the reaction mechanism. This behavior will be examined in the Discussion. The efficiency must, of course, be high at all times in view of the production of steam as a result of a nuclear accident.

The air purge that immediately followed the dose of 120 minutes showed a very interesting and significant behavior. It has already been shown that many new charcoals, and those with limited service, exhibit a sharp drop in ^{127}I-CH$_3$ concentration immediately after the dose was completed. In contrast, the effluent concentration from exhausted carbons continued to increase after the dose period, reached a maximum, and then slowly decreased in concentration until it approached the initial base line of the detector.

The purge behaviors for the three tests described in Table 10 are shown in the graphs of Figure 9 and that at 30% RH in Figure 10. The effluent concentration continued to rise and the maximum for Test 3318 (subjected to prehumidification) was 3.2 mg/M^3 at 170 minutes. The maximum for Test 3332 (without prehumidification) was 2.60 mg/M^3 at 230 minutes. The emission of ^{127}I-CH$_3$ in the air purge in Test 3339 at 30% RH began slowly but a maximum of 0.50 mg/M^3 was observed at 1700 minutes. The summation of the ^{127}I-CH$_3$ in the effluents (Table 11)
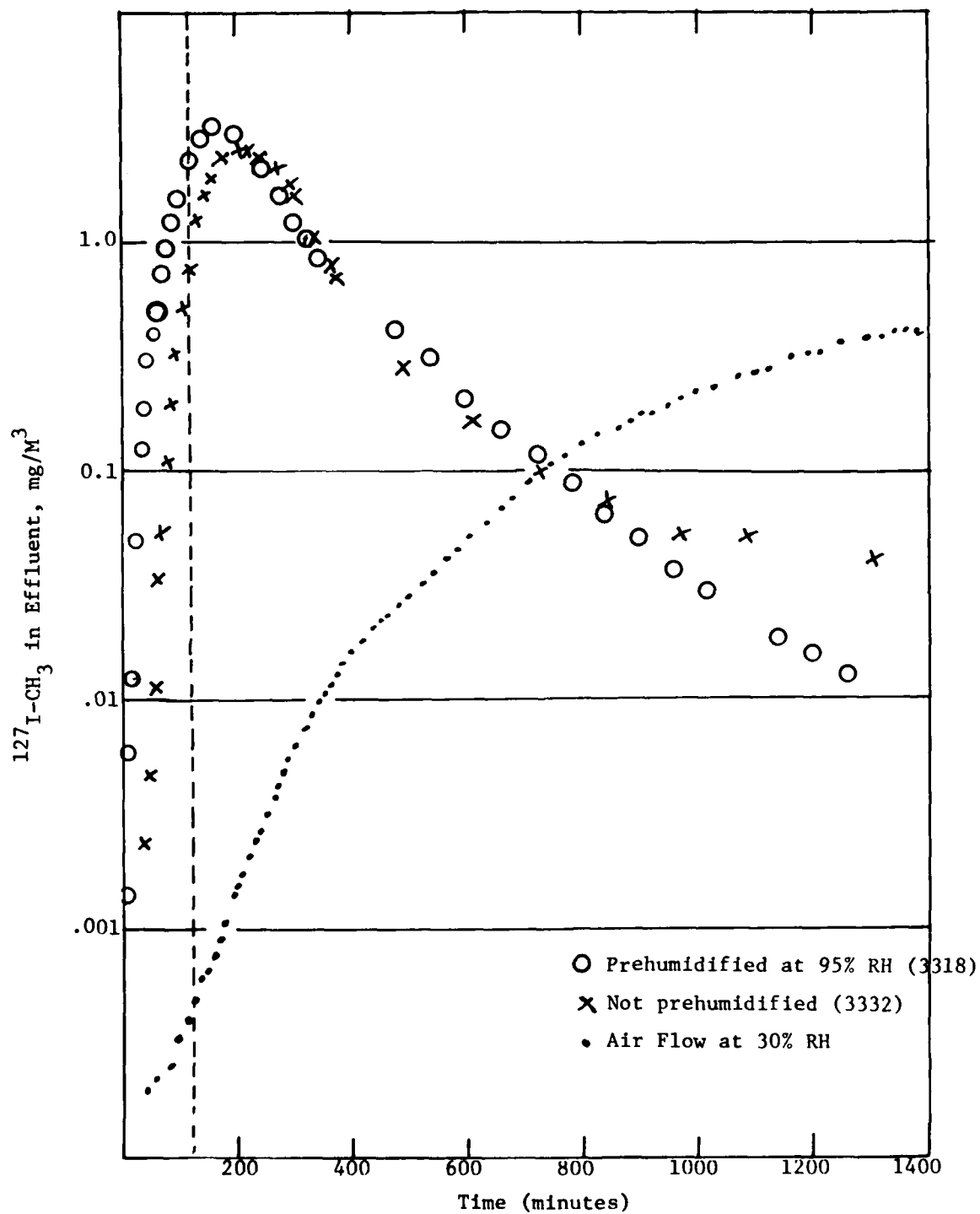
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Figure 9. $^{127}I-CH_3$ in effluent (mg/M^3) for the three charcoals of Table 9.

⊙ - 3318 prehumidified
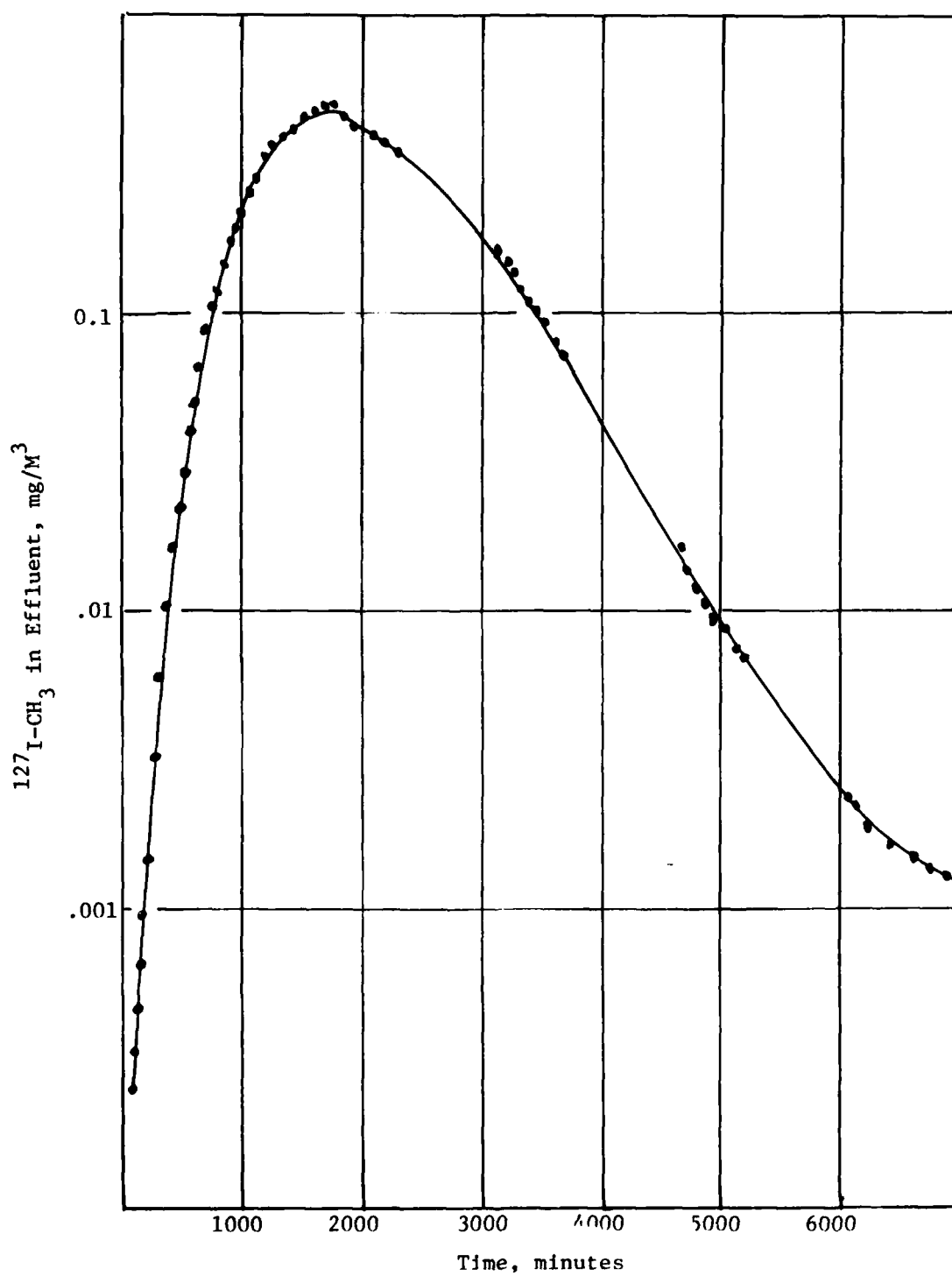X - 3332 not prehumidified
● - 3339 with air at 30% RH

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Figure 10. ^{127}I-CH$_3$ in effluent (mg/M^3) for the prolonged (5 days) purge at 30% RH.

indicates a high recovery of the dose. The total was 94% for both runs
at 95% RH and 69% for the run at 30% RH.

Table 11: Emission of ^{127}I-CH$_3$ during the Air Purges of NRL Sample 5144

| Test | Location of Maximum | | Total Purge | | Total | Recovery |
	Time (min)	Concn. (mg/M^3)	Duration (min)	Total (mg)	Dose (mg)	(%)
3318	170	3.2	1200	3.54	3.76	94.
3332	230	2.60	1300	3.12	3.34	93.
3339	1700	0.50	7000	5.48	7.92	69.

It may be concluded that the charcoal in an exhausted carbon filter
behaves like a chromatographic column. The retention is least in the
air flow of 95% RH. While the emission at 30% RH is high (69%), the
average concentration during the purge is least due to the large volume
of air (43 M^3) required to attain the base line reading.

The question arose in the above experimentation as to the possi-
bility of some regeneration after an extensive air purge as used in the
above experiments. The above Test 3332 was repeated after the purge
and without removing the sample from the container. The penetration
using the second dose of the same value was followed for 60 minutes
(Figure 11) and the results established that no regeneration had taken
place by virtue of an air purge alone. This observation warrants further
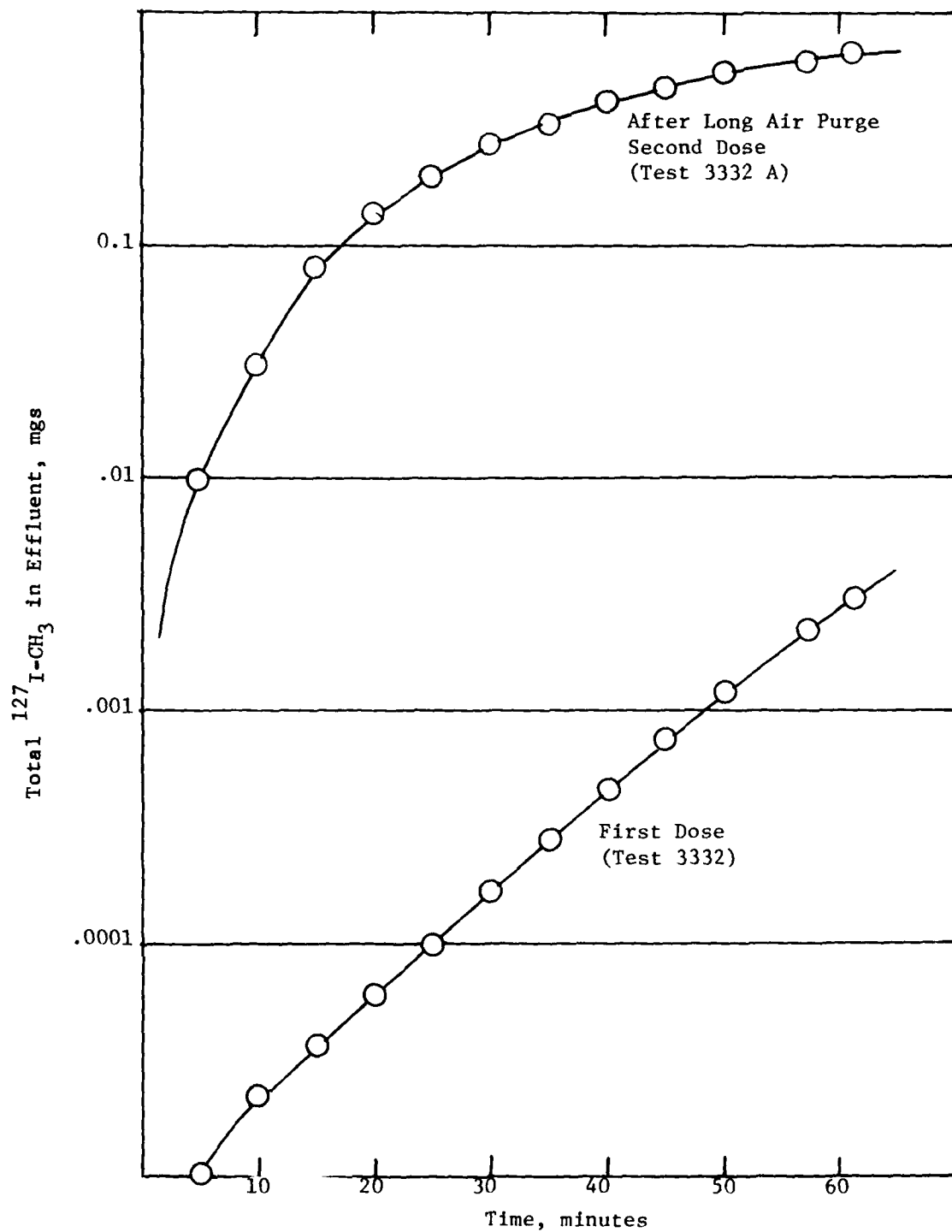experimentation under a variety of relevant conditions.

Figure 11. Repeat test 3332A conducted after the extended purge of Test 3332.

V. Discussion

The objective of a carbon filter test using ^{127}I-CH$_3$ as the insult is to derive information on the residual trapping efficiency. This is a pre-accident factor of prime importance. As pointed out in the Introduction, the chromatographic measurement of ^{127}I-CH$_3$ by the electron capture detector is blind to the presence of radioiodine; but, conversely, the use of ^{131}I-CH$_3$ and the necessary counting technique is blind to the part played by the surface chemical reactions in the iodized (^{127}I) carbons.

The experimental facts described in this report may be summarized as follows:

(1) A reproducible precision better than 10^{-3} ppm in concentration of ^{127}I-CH$_3$ was realized using chromatography with electron capture detection. It can be used to determine the ^{127}I-CH$_3$ in the effluents from a test conducted according to the RDT M16 test conditions (dose = 1.75 mg/M^3) and to obtain penetration values as low as 0.001%.

(2) Independent determinations with new carbons gave similar penetration values at 120 minutes when using ^{127}I-CH$_3$ (by chromatography) or with ^{131}I-CH$_3$ (by counting).

(3) The concentration of ^{127}I-CH$_3$ in the air purge at the completion of the dose using many new or slightly used carbons drops rapidly to base line values, indicating the complete retention of ^{127}I-CH$_3$. This behavior agrees with the ^{131}I-CH$_3$ test for the same carbon.

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(4) A chromatographic behavior develops with iodized carbons after the carbon bed was continuously used under routine service conditions. The concentration of effluent ^{127}I-CH$_3$ increased to a maximum value after the dose period and then slowly decreased to base line values.

(5) The total effluent ^{127}I-CH$_3$ from tests with an exhausted charcoal at 95% RH with either prehumidification or no prehumidification were the same. Lowering the relative humidity to 30% appeared only to extend the time required to desorb the ^{127}I-CH$_3$ (see Table 11). It appears that a high relative humidity and/or prehumidification promote early elution.

(6) Prolonged air flows at 30°C did not appear to regenerate a used carbon to any significant extent. The second dose of ^{127}I-CH$_3$ under test conditions after purging showed a much greater penetration than observed during the first dose (Figure 11).

(7) The ^{131}I-CH$_3$ penetration using long-service carbons is somewhat less than the ^{127}I-CH$_3$, but the magnitude of either is above 10% which is not an acceptable performance.

The pioneering studies at the Oak Ridge National Laboratories (12, 13, 14) in 1965-1966 lead to the following postulated isotopic exchange with charcoals impregnated with one or more iodine-containing substances:

$$^{131}\text{I-CH}_3 + {}^{127}\text{I(on charcoal)} \rightarrow {}^{127}\text{I-CH}_3 + {}^{131}\text{I(on charcoal)}$$
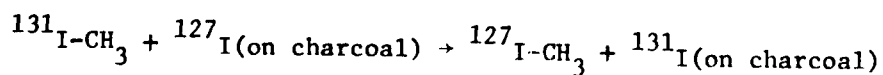
Ackley, Adams and Browning (12) stated:

". . . . when molecules of $CH_3{}^{131}I$ enter the charcoal bed, they encounter non-radioactive ^{127}I atoms of the impregnant. Some of the encounters result in exchange of the two types of iodine atoms. Thus, the methyl iodide that is radioactive when it enters the charcoal tends to be transformed into non-radioactive methyl iodide which ultimately emerges downstream of the charcoal while a corresponding amount of the radioactivity remains behind."

Measurements at the Oak Ridge Laboratory were reported in 1966 (14) using two types of detection for methyl iodide at the same time with the iodized charcoal MSA 85851. The results are summarized (Table 12) for the penetration (%) in carbon columns 1" diameter, 2" depth, 40 fpm linear velocity, temperature 24°C, sample prehumidified at the relative humidity noted, and for a total dose of 0.1 mg $^{127}I-CH_3$ in a 2-hour feed period. The gas chromatograph results are for the effluent sampled at the time specified; the $^{131}I-CH_3$ count was automatically integrated over the entire duration of the test. Integration of the chromatographic data would have decreased the reported value for penetration, but not to the low value reported for the $^{131}I-CH_3$ counting.

One argument opposing the above simplistic model of isotope exchange is the fact that $^{127}I-CH_3$ itself can also be completely trapped with some, but not all new iodized charcoals as shown in the present investigations. As already pointed out, the ratio of ^{131}I to the ^{127}I carrier in practical test dosages is about 10^{-15}. If all of the ^{131}I were exchanged, it would be extremely difficult with the present detector to observe the tiny increase in $^{127}I-CH_3$ over that in the carrier quantity.

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Table 12: Penetration (%) Through MSA 85851 Impregnated Charcoal
(1" diameter, 2" depth, linear velocity of 40 fpm,
temperature 24°C, total dose of 0.1 mg ^{127}I-CH$_3$ in
2 hours, prehumidified)
[From the Oak Ridge Report ORNL - 3915 (14)]

Time (hrs)	MSAC-1 71% RH	MSAC-2 71% RH	MSAC-3 71% RH	MSAC-5 <3% RH
	^{127}I-CH$_3$ (gas chromatograph at specified time, i.e. not integrated			
0.83	22	–	–	–
2.0	54	–	–	–
4.0	100	43	54	0.6
5.0	–	–	–	6.0
	^{127}I-CH$_3$ + ^{131}I-CH$_3$ (count integrated for given period			
6	–	0.35	–	–
7	–	–	0.33	–
72	–	–	–	0.03

The Oak Ridge results with the carbon MSA 85851 and those previously
reported by the authors (1) at the 15th DOE Air Cleaning Conference
demonstrate the lack of stability of some new iodized charcoals after
contact with methyl iodide. Some ^{127}I-CH$_3$ continued to be purged
after the 120-minute dosing period. The sample of BC-727 (1) that
showed methyl iodide in the air purge had been previously used and
this could have been responsible for the reported purge behavior.
However, the three carbons 4314, 4315 and 4316 (see Appendix 1) had
the same laboratory impregnations on three different coal-base carbons
and showed variable purge behavior. The different behavior of iodized
carbons even when new demonstrates the complex chemistry of the iodine-
charcoal system. Unpublished results in this Laboratory have shown

considerable variability among base carbons for retaining elementary iodine. Methyl iodide has been found to be present in the air flow and in increasing amounts as the carbon-iodine sample is heated slowly above ambient.

In the design of a ^{131}I-CH$_3$ removal system, Ackley, Adams and Browning (12) recommended some provision that would maintain the prevailing relative humidity below 90% RH. A simple procedure to accomplish this would be to pre-warm the air flow to the carbon. To reduce 95% RH air at 77°F to 50% RH requires a temperature increase of 18°F and to reduce 95% RH air to 70% RH requires 9°F. The disadvantage is, of course, the heating costs of the large volume of air in process. Heating estimates to reduce the relative humidity of inlet air for time periods at designated relative humidities and to reach target values of 70 or 50% RH are summarized in Table 13. Since the inlet air is not always at 95% RH, some consideration should be given to the controlled use of heaters on ventilating systems based on specific technical and economic analysis.

Table 13: Heating Estimate to Reduce the Relative Humidity of Inlet Air to Either 50 or 70% RH for a Carbon Unit of 30,000 CFM

Fraction of Inlet Air at Designated Relative Humidity			Required Heat (BTU) to Reach Designated Target	
95% RH	70% RH	50% RH	50% RH	70% RH
1.0	0	0	3.96×10^9	1.98×10^9
.5	.5	0	2.97×10^9	0.99×10^9
.25	.5	.25	1.98×10^9	0.50×10^9
.20	.4	.40	1.58×10^9	0.40×10^9
.10	.40	.50	1.18×10^9	0.20×10^9

Although many of the carbon systems now installed in nuclear plants have in-line heaters that could be used for the above purpose, the heaters are used chiefly to prepare a carbon filter for a freon leak-test. It is necessary to decrease the water-content of the carbon in order to realize a suitable freon adsorption for the leak-test.

The strong influence of relative humidity on methyl iodide trapping, either in prehumidification or that contained in the air during the dose of methyl iodide, is evidence of another important parameter. Ackley, Adams and Browning (12) pointed out the adverse influence of high relative humidity on methyl iodide trapping and they associated the decrease in efficiency with the corresponding increase in water adsorption by the carbon. It is a fact, however, that the efficiency of TEDA impregnated activated carbons are not impaired at high relative humidities as are iodized carbons using the same base charcoals. It is not likely in TEDA-containing carbons that the isotope exchange suggested in the above equation is the mode of operation. However, the addition of $^{131}I-CH_3$ or $^{127}I-CH_3$ to the triethylenediamine molecule (TEDA) can form an alkyl ammonium salt linkage. The negative iodide ion can then undergo isotope exchange. The $^{127}I-CH_3$ used with the $^{131}I-CH_3$ dose in a test procedure can thus interact in several ways. A more comprehensive understanding must consider the interface of the charcoal and impregnant, the adsorbed water and the gaseous iodine species.

According to current concepts, isotope exchange between a gas and a solid takes place via an activated surface complex. The presence of an isotope mixture is not required for the formation of the surface complex.

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Gas molecules in a mixture of ^{131}I-CH$_3$, ^{125}I-CH$_3$, or ^{127}I-CH$_3$ react at the same rate to form the same transition complex; in other words, the chemistry is independent of the isotopic composition. Since the rates of these chemical reactions are independent of the isotope species, a considerable scrambling of the iodine isotopes can be anticipated and the penetration composition would contain all possible isotopes in proportion to the concentration at the reactive site.

Preliminary experiments to be reported elsewhere and using the three iodine species ^{125}I, ^{127}I, and ^{131}I have demonstrated that considerable scrambling of the iodine isotope does indeed take place during a penetration test of iodized carbons. It is possible to gasify ^{125}I and ^{131}I, previously placed in the iodized carbon, by contact with ^{127}I-CH$_3$ in the air flow. The concentrations, flow rates, temperature, and relative humidity were those specified in the RDT M16 test procedures. It may also be noted that at Oak Ridge (14) when the MSA 85851 charcoal was tagged with ^{128}I ($t_{1/2}$ = 25 min) by neutron irradiation of the ^{127}I impregnation, the effluent contained ^{128}I-CH$_3$ when ^{127}I-CH$_3$ was introduced.

There appears to be a fundamental difference in the mode of methyl iodide removal by new or slightly used iodized carbons and that by the carbons which have seen service in ventilating systems. The change is progressive and must be considered in the development of in-place testing of carbon filters.

In the case of new carbons, it has been found (16) that the fractional penetrations of ^{131}I-CH$_3$ in each of equal volume sections of a column were the same. The constant penetration fraction, through each of the eight sections in which the various columns were divided, is shown in Table 14. The behavior is in accord with a catalytic mechanism

Table 14: Fractional Penetration of ^{131}I-CH$_3$ Through the Individual Sections at Designated Linear Flow Rates Using New Carbons (16)

Charcoal 4167

$V_1(cm \cdot s^{-1})$	13.8	22.7	31.6	63.1
1	0.382	0.551	0.687	0.800
2	0.386	0.566	0.716	0.833
3	0.374	0.570	0.708	0.836
4	0.386	0.547	0.700	0.835
5	0.362	0.538	0.694	0.841
6	0.389	0.556	0.667	0.844
7	0.478	0.572	0.672	0.847
8	0.427	0.505	0.654	0.850
Mean	0.398	0.551	0.687	0.836
Standard deviation	±0.037	±0.022	±0.021	±0.016

Charcoal 4171

$V_1(cm \cdot s^{-1})$	21.1	31.6	44.6	63.1	84.9
1	0.744	0.722	0.679	0.648	0.595
2	0.760	0.741	0.685	0.646	0.654
3	0.744	0.745	0.665	0.663	0.626
4	0.749	0.731	0.667	0.637	0.619
5	0.760	0.747	0.654	0.636	0.618
6	0.756	0.739	0.641	0.616	0.605
7	0.750	0.746	0.639	0.615	0.553
8	0.758	0.736	0.636	0.602	0.513
Mean	0.753	0.738	0.658	0.633	0.598
Standard deviation	±0.007	±0.009	±0.019	±0.020	±0.045

Charcoal 4169

$V_1(cm \cdot s^{-1})$	4.52	9.05	14.8	20.6	41.1
1	0.424	0.573	0.661	0.735	0.794
2	0.452	0.589	0.662	0.743	0.796
3	0.437	0.636	0.672	0.743	0.768
4	0.557	0.529	0.690	0.747	0.760
5	0.384	0.460	0.680	0.723	0.775
6	0.332	0.591	0.662	0.723	0.772
7	0.539	0.493	0.636	0.727	0.752
8	0.406	0.513	0.646	0.712	0.785
Mean	0.441	0.548	0.664	0.732	0.775
Standard deviation	±0.075	±0.059	±0.017	±0.012	±0.016

and indicates a steady-state reaction in which the concentration attenuation in the column at constant flow does not depend on time.

The above behavior was not found for carbon that had seen service. When impregnated carbons were exposed to outdoor air for various time periods in equal volume sections (each 0.5 inch depth) and the penetration of ^{131}I-CH$_3$ then determined for each section, the fractional penetration through each was not constant. A large number of examples have been reported (17) and typical behaviors are given in Table 15. The inlet segment of the column always suffered the greatest penetration in its role of a guard layer and the remaining segments of the carbon bed gave varying concentration attenuation. The behavior of exposed charcoals suggests an adsorption-desorption model for ^{131}I-CH$_3$ penetration because the flow (time) depends on concentration attenuation. It has been found that as the exposure is lengthened, the concentration attenuation is greater and the total penetration gradually increased.

Table 15: Fractional Penetration of ^{131}I-CH$_3$ Through Four Sequential Sections of Impregnated Carbons Weathered in Outdoor Air Flow

Section	G 615	G 615	BC 727	BC 727
1	.365	.430	.404	.491
2	.283	.339	.331	.401
3	.241	.305	.287	.419
4	.289	.318	.338	.431
Penetration	.0072	.0141	.0130	.0356

There appears to be a continuous transition, therefore, from a catalytic behavior in new or slightly used iodized carbons to an adsorption-desorption model as the carbons are subjected to extended

service. An isotope exchange is apparently more probable during a
catalysis in which a carbon-iodine bond may be broken or weakened than
in an adsorption-desorption process in which the molecule of methyl
iodide remains intact. Some fundamental experimentation is required
to elucidate this model in greater detail; the equipment to do this is
available at NRL.

The time-dependent release of ^{131}I is tabulated in the Rogovin
Report (18) for the Three Mile Island accident of 28 March. The source
data were those given in the TDR-TMI-116 Report of 31 July 1979. These
results present an opportunity to test the considerations set forth as
Case I, Case II and Case III of the Introduction.

The monitor at Three Mile Island was located in the stack of Unit 2
which received all effluent from the iodized carbon filters until it was
capped in early May 1979. The data in Table 2.2 (Volume II, Part 2,
Rogovin Report) can be used to calculate the rates (Curie/hour) of ^{131}I
release and the rates are plotted in Figure 12 as Y-coordinate with the
total elapsed time from 28 March as X-coordinate. The initial iodine
release and the 25-hour period thereafter may be considered as a dose
period to the carbon filters; the subsequent 900 hours to 2 May is the
air purge at a total flow of 10^5 CFM. There is a striking resemblance
between the ^{131}I "bleeding" or penetration at Three Mile Island and the
behavior observed (Figure 10) in the laboratory with ^{127}I-CH$_3$ for which
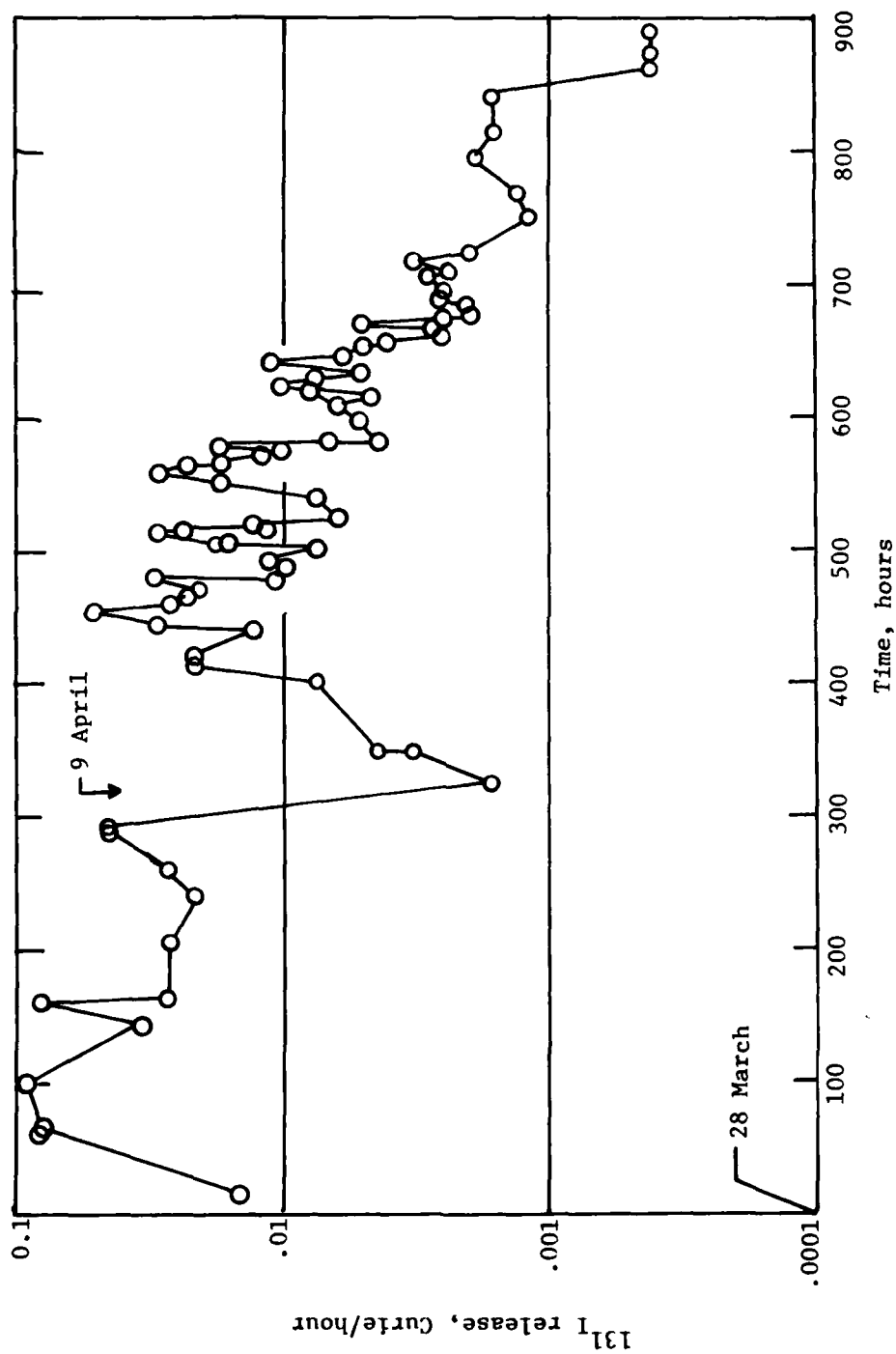the air purge was followed for five days.

Figure 12. The rate of release of ^{131}I in the Three Mile Island accident as a function of the total time after 28 March 1979 (18).

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The interpretation of the observations and measurements in the
early days after March 28th is not too straightforward. In a careful
analysis, Cline, Voilleque, Pelletier and Thomas (19) concluded that
the bulk of the iodine was evolved and deposited during the early part
of the accident, possibly during the first day. Their thesis agrees
with the above postulate that the major insult to the carbon filters
could have taken place during this period. The subsequent "bleeding" of
^{131}I set forth in Figure 12 was augmented to a lower degree by the added
dose due to the slow gasification of ^{131}I from the surfaces of the various
items in the containment space and duct work. There has been a major
drop in ^{131}I emission after the stack was sealed which directed all
effluent through the new carbon beds installed on the roof. The results
used in Figure 12 were based on measurements made before the new carbon
beds were placed in service.

VI. Concluding Remarks

1. Laboratory results obtained with ^{127}I-CH$_3$ on-line testing of iodized carbon from filters in service show that the observed reductions in trapping efficiency with service are accompanied by the appearance of ^{127}I-CH$_3$ in the effluent air after the dose period. This behavior with ^{131}I-CH$_3$ has escaped notice due to the way the test is made. In order to obtain equivalent data with ^{131}I-CH$_3$, the cost would be prohibitive at the current test charge per point (~$400/test).

2. A postulated lifetime behavior of an iodized carbon filter is shown in Figure 13. The lowest curve corresponds to new carbon and carbon with limited service. In an upward sequence, the carbon has been weathered for 3 months, 6 months, 1 year, and 4 years. Since the carbon filter must be ready to play its role at any time in advent of an accident, it is most important to know the current stage of a filter. The service times will vary with solvent spills, excessive moisture as well as with the usual contaminants of the air.

3. The chromatographic hold-up of ^{127}I-CH$_3$ by carbons in service, together with the subsequent slow desorption step, could result in a dilution of the penetrating iodine to acceptable levels under some conditions encountered in filter operations.

4. Since testing procedures using ^{131}Iodine have been pursued in the presence of 10^{15}-fold excess of ^{127}I in the gas phase, the question remains what would happen in a carbon filter in an accident mode when subjected to 100% ^{131}I. It is suggested that the results would resemble those reported herein using the ^{127}I species as the test gas. The
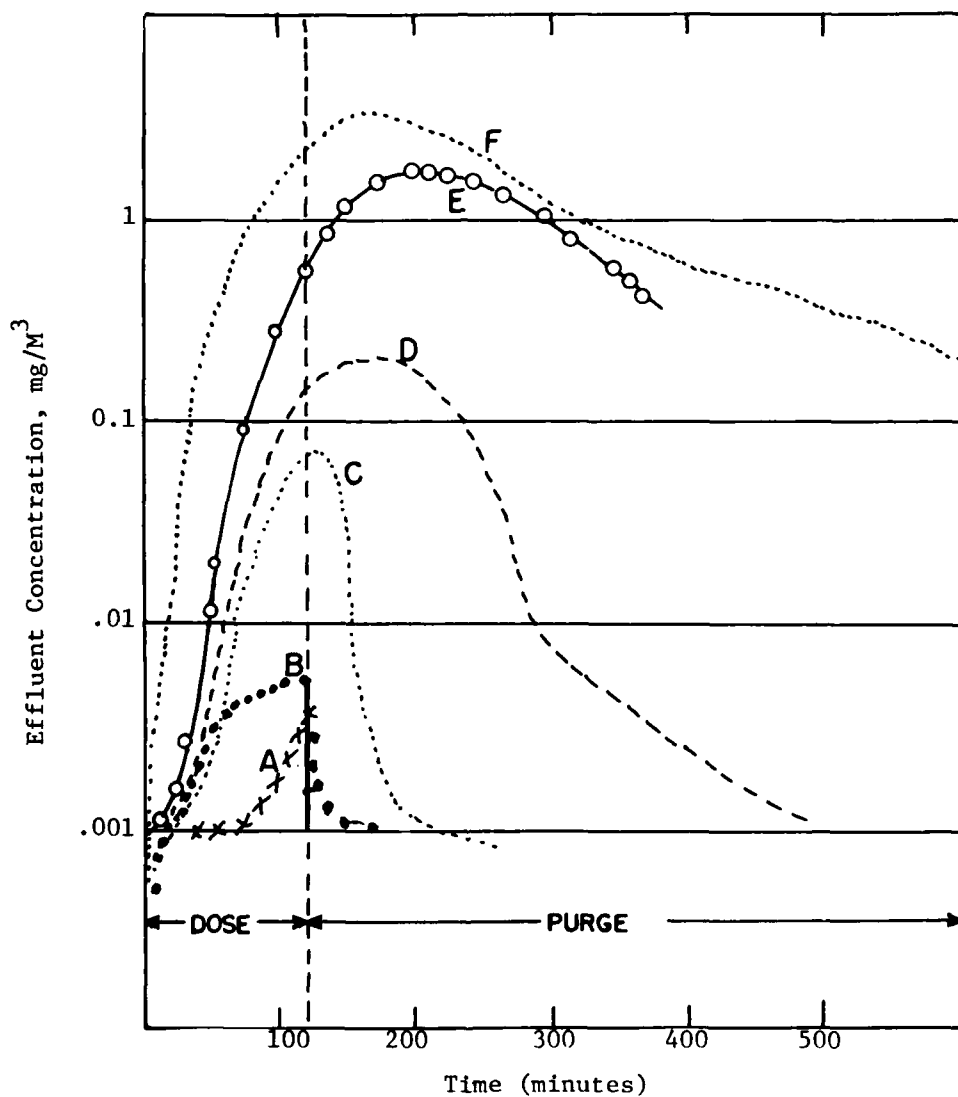
Figure 13. Postulated life-time behavior of iodized carbon filters in the penetration of ^{127}I-CH_3.

A – new at 120 min   D – one year
B – three months   E – removed at utility
C – six months   F – removed at utility

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behavior of the carbon filters at Three Mile Island (Figure 12) and the laboratory behavior with ^{127}I-CH$_3$ as the test species (Figure 10) substantiate this thesis.

ACKNOWLEDGEMENT

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Appendix 1: Summary of Charcoals Studied in this Report

Notation	Base Charcoal	Impregnation
BC 727	Coconut	$KI + xI_2 = KI_x$
NACAR 615	Coconut	KI and TEDA
NRL 4314	Coal, ACC	$KIO_3 + KI + K_3PO_4 +$ HMTA
NRL 4315	Coal, 207A	ditto
NRL 4316	Coal, BPL	ditto
NUCON KITEG II	Coconut	
NRL 5022	Coconut	NACAR 615, weathered three months
NRL 5149	Coconut	KI_x, from utility operation
NRL 5144	Coconut	KI_x, from utility operation
NRL 4167	Coconut	I_2, NaOH and HMTA
NRL 4169	Coal base	ditto
NRL 4171	Coconut	ditto

BC 727	8 x 16, Barnebey Cheney
NACAR 615	8 x 16, North American Carbon Inc.
ACC	6 x 14, Columbia Activated Carbon
207A	8 x 16, Sutcliffe, Speakman Co. Ltd.
BPL	8 x 20, Activated Carbon Division, Calgon Corp.
KITEG II	Nuclear Consulting Services, Inc.
TEDA $\equiv$	triethylenediamine
HMTA $\equiv$	hexamethylenetetramine